

Radiation-curable compounds based on 2,4-diethyloctanediol

Conventionally, free-radically or cationically copolymerizable compounds are used as coating compositions. Those suitable in principle are compounds of high, or relatively high, molecular mass which following application can easily be cured, for example by irradiation with high-energy light, to give coatings having satisfactory mechanical properties. However, the viscosity of these compounds must not be too high, since it must ensure ease of application and good distribution on the surface that is to be coated. For this reason, it is common to use low molecular mass, free-radically or cationically polymerizable compounds as reactive diluents in a mixture with compounds of higher molecular mass in order to both ensure good flow of the coating compositions and good mechanical properties, such as hardness and elasticity, in the cured coating.

It is therefore an object of the invention to provide compounds suitable as reactive diluents in polymerizable compositions, especially radiation-curable compositions.

We have found that this object is achieved by compounds formed from an alcohol a) and from one or more components b) reactive with the alcohol, wherein alcohol a) is selected from 2,4-diethyloctane-1,5-diol and derivatives thereof alkoxylated with ethylene oxide, propylene oxide or mixtures thereof, and at least one of the components b) reactive with the alcohol is an organic compound b₁) having up to 30 carbons and at least one ethylenically unsaturated, free-radically or cationically copolymerizable group.

We have also found radiation-curable compositions which comprise these compounds, and the use of these compounds as reactive diluents.

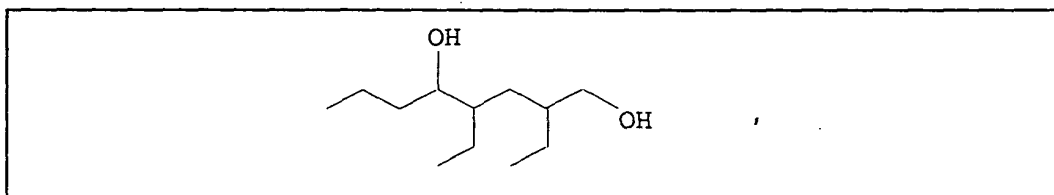
The novel compound is a product of the reaction of the alcohol a) with component b), it being possible for both or just one of the hydroxyls of the alcohol a) to be reacted with b).

In the reaction product preferably both hydroxyls of the alcohol a) have reacted with the organic compound b₁).

Also suitable are compounds where only one of the hydroxyls is reacted with the organic compound b₁).

Other suitable compounds are those where one of the hydroxyls of the alcohol a) has reacted with the organic compound b₁) and the other hydroxyl has reacted with a noncopolymerizable organic compound having preferably likewise up to 30 carbons, in particular up to 15 carbons. Examples of the latter compound are saturated aliphatic or aromatic carboxylic acids which form an ester with the hydroxyl of a), or aliphatic or aromatic epoxy compounds which form a b-hydroxy compound with the hydroxyl.

The alcohol a) is 2,4-diethyloctane-1,5-diol of the formula



whose hydroxyls may have been alkoxyated with ethylene oxide (EO) or with propylene oxide (PO) or with mixtures thereof.

The degree of alkoxylation of the hydroxyls, defined as the number of EO and PO units per hydroxyl, is preferably from 0 to 10, in particular from 0 to 5 and, with particular preference, from 0 to 3.

2,4-Diethyloctane-1,5-diol is known per se, for example from JP 05229973.

As is known, the alkoxyated derivatives can be obtained by reacting 2,4-diethyloctane-1,5-diol with the desired amounts of ethylene or propylene oxide.

b₁) is preferably a carboxylic acid, a carbonyl halide or a carboxylic anhydride, which reacts with the alcohol a) to form an ester or diester.

b₁) may also be acetylene or acetylene derivatives, which react with a) to give the corresponding vinyl ethers.

b₁) is preferably an organic compound of not more than 20 carbons, and with particular preference not more than 15 carbons.

The organic compound b₁) may contain one or more, for example two or three, ethylenically unsaturated, free-radically or cationically

copolymerizable groups; preferably, b_1) contains one such group.

b_1) is preferably acrylic, methacrylic, itaconic or maleic acid or acetylene.

Depending on the chemical nature of b) and/or b_1), preparation of the novel compound from a) and b) takes place by customary esterification or vinylation.

Preferred novel compounds are:

2,4-diethyloctane-1,5-diol divinyl ether, 2,4-diethyloctane-1,5-diol diacrylate, 2,4-diethyloctane-1,5-diol dimethacrylate, and the corresponding acrylic and/or methacrylic esters of the alkoxyated alcohol a) where the degree of alkoxylation of the OH groups can in each case be from 0 to 3 and where preferably 1 to 3 alkoxy groups are present in total in the compound.

The novel compound is suitable as a reactive diluent in radiation-curable compositions in which curing (polymerization) of the free-radically or cationically polymerizable compounds can take place photochemically.

The content of the novel compound in these compositions can be from 0.5 to 100 % by weight, based on the overall amount of the polymerizable compounds.

The proportion of the novel compound is preferably not less than 1 % by weight, with particular preference not less than 5 % by weight, and not more than 70 % by weight, with particular preference not more than 50 % by weight, based on the overall amount of free-radically polymerizable compounds in these compositions.

Examples of other suitable polymerizable compounds in the above compositions include compounds having an ethylenically unsaturated copolymerizable group.

Examples which may be mentioned are C_1 - C_{20} -alkyl (meth)acrylates, vinylaromatic compounds having up to 20 carbons, vinyl esters of carboxylic acids having up to 20 carbons, vinyl alcohols, ethylenically unsaturated nitriles, vinyl ethers of C_1 - C_{10} alcohols and C_2 - C_8 aliphatic hydrocarbons with 1 or 2 double bonds.

Preferred alkyl (meth)acrylates are those with a C_1 - C_{10} -alkyl, such as methyl methacrylate and methyl, n-butyl, ethyl and 2-ethylhexyl acrylate.

Also suitable, in particular, are mixtures of alkyl (meth)acrylates.

Examples of vinyl esters of C_1 - C_{20} carboxylic acids are vinyl laurate, stearate, propionate and acetate, vinyl alcohol as well being obtained therefrom by hydrolysis.

Examples of suitable vinyl aromatic compounds are vinyltoluene, α -butylstyrene, 4-n-butylstyrene, 4-n-decylstyrene and, preferably, styrene.

Examples of nitriles are acrylonitrile and methacrylonitrile.

Examples of suitable vinyl ethers are vinyl methyl, isobutyl, hexyl and octyl ether.

C_2 - C_8 nonaromatic hydrocarbons with one or two olefinic double bonds which may be mentioned are butadiene, isoprene, and also ethylene, propylene and isobutylene.

Preferred further polymerizable compounds are those with two or more polymerizable, ethylenically unsaturated groups, especially (meth)acrylate compounds.

Suitable (meth)acrylate compounds contain 2 to 20, preferably 2 to 10 and, with particular preference, 2 to 6 copolymerizable, ethylenically unsaturated double bonds.

The number-average molecular weight M_n of these (meth)acrylate compounds B) is preferably below 15,000, more preferably below 5000 and, with particular preference, below 3000 g/mol and more than 180 g/mol (as determined by gel permeation chromatography with polystyrene as standard and tetrahydrofuran as eluent).

Possible (meth)acrylate compounds are (meth)acrylates and, in particular, acrylates of polyfunctional alcohols, especially those which other than the hydroxyls contain no other functional groups, or at best ether groups. Examples of such alcohols are bifunctional alcohols, such as ethylene glycol, propylene glycol and their counterparts with higher degrees of condensation, such as diethylene

glycol, triethylene glycol, dipropylene glycol, tripropylene glycol, etc., butanediol, pentanediol, hexanediol, neopentyl glycol, alkoxyated phenolic compounds, such as ethoxyated and/or propoxyated bisphenols, cyclohexanedimethanol, alcohols with a functionality of three or more, such as glycerol, trimethylolpropane, butanetriol, trimethylolethane, pentaerythritol, ditrimethylolpropane, dipentaerythritol, sorbitol, mannitol and the corresponding alkoxyated alcohols, especially ethoxyated and propoxyated alcohols.

The alkoxylation products can be obtained in a known manner by reacting the above alcohols with alkylene oxides, especially with ethylene or propylene oxide. The degree of alkoxylation per hydroxyl is preferably from 0 to 10; in other words, 1 mol of hydroxyl can preferably be alkoxyated with up to 10 mol of alkylene oxides.

Other possible (meth)acrylate compounds are polyester (meth)acrylates, which are the (meth)acrylic esters of polyesterols.

Examples of suitable polyesterols are those which can be prepared by esterifying polycarboxylic acids, preferably dicarboxylic acids, with polyols, preferably diols. The starting materials for such hydroxyl-containing polyesters are known to the skilled worker. Preferred dicarboxylic acids used are succinic, glutaric, adipic, sebacic and o-phthalic acid, their isomers and hydrogenation products, and also esterifiable derivatives, such as anhydrides or dialkyl esters, of said acids. Suitable polyols are the abovementioned alcohols, preferably ethylene glycol, 1,2- and 1,3-propylene glycol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, cyclohexanedimethanol and also polyglycols of the ethylene glycol and propylene glycol type.

Polyester (meth)acrylates can be prepared in two or more stages or else in a single stage, as described in EP 279 303, for example, from acrylic acid, polycarboxylic acid and polyol.

Examples of further possible (meth)acrylate compounds are epoxy or urethane (meth)acrylates.

Epoxy (meth)acrylates, for example, are those compounds as obtainable by reacting epoxidized olefins or poly- or mono- or diglycidyl ethers, such as bisphenol A diglycidyl ether, with (meth)acrylic acid.

The reaction is known to the skilled worker and is described, for example, in R. Holmann, U.V. and E.B. Curing Formulation for Printing Inks and Paints, London 1984.

The urethane (meth)acrylates are, in particular, reaction products of hydroxyalkyl (meth)acrylates with poly- or diisocyanates (see again R. Holmann, op. cit.).

It is of course also possible to employ mixtures of different compounds, especially mixtures of the above (meth)acrylate compounds.

Examples of further suitable polymerizable compounds are unsaturated polyester resins, consisting essentially of polyols, especially diols, and polycarboxylic acids, especially dicarboxylic acids, where one of the esterification components contains a copolymerizable, ethylenically unsaturated group. Examples of such compounds are maleic or fumaric acid or maleic anhydride.

The novel compounds are particularly suitable as reactive diluents for radiation-curable compositions based on epoxy acrylates, for example bisphenol A diglycidyl ether diacrylate.

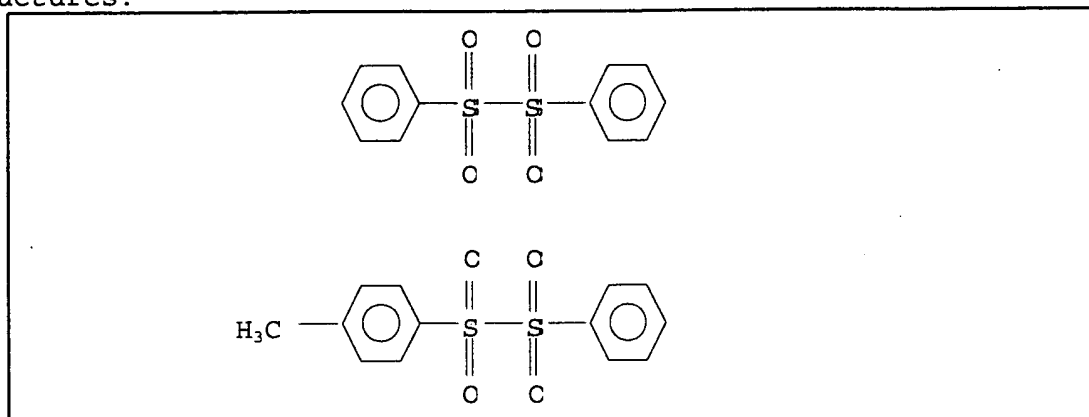
In the case of radiation curing by UV light a photoinitiator is preferably added to the radiation-curable compositions.

The overall amount of photoinitiator is preferably from 0.1 to 10 % by weight, with particular preference from 0.5 to 5 % by weight, based on the overall amount of the free-radically or cationically polymerizable compounds in these compositions.

Examples of suitable photoinitiators for the free-radical polymerization are benzophenone and derivatives thereof, examples being alkylbenzophenones, halomethylated benzophenones, Michler's ketone, and also benzoin and benzoin ethers, such as ethyl benzoin ether, benzil ketals, such as benzil dimethyl ketal, acetophenone derivatives, such as hydroxy-2-methyl-1-phenyl- propan-1-one and hydroxycyclohexyl phenyl ketone, anthraquinone and its derivatives, such as methyl anthraquinone and, in particular, acylphosphine oxides, for example Lucirin TPO (2,4,6-trimethylbenzoyldiphenylphosphine oxide) and bisacylphosphine oxides.

Photoinitiators for the cationic polymerization give acids on irradiation with UV light; examples which may be mentioned include

aryldiazonium, aryliodonium or arylsulfonium salts, disulfones, diazo disulfones, imido triflates and benzoin tosylates of the following structures:



Mention may also be made, by way of example, of p-methoxybenzenediazonium hexafluorophosphate, benzenediazonium tetrafluoroborate, toluenediazonium tetrafluoroarsenate, diphenyliodonium hexafluoroarsenate, triphenylsulfonium hexafluorophosphate, benzenesulfonium hexafluorophosphate, toluenesulfonium hexafluorophosphate or Degacure KI85 (bis[4-diphenylsulfoniophenyl] sulfide bis-hexafluorophosphate), isoquinolinium salts, phenylpyridinium salts or picolinium salts, for example N-ethoxyisoquinolinium hexafluorophosphate, N-ethoxy-4-phenylpyridinium hexafluorophosphate or N-ethoxy-2-picolinium hexafluorophosphate. Also suitable are ferrocenium salts (for example, Irgacure 261 from Ciba) or titanocenes.

To produce coatings, the radiation-curable compositions are applied to the substrates that are to be coated, consisting for example of wood, paper, plastic or metal, and may include the additives customary for the particular application, for example leveling agents, reinforcers, pigments or fillers.

Examples of possible uses which may be mentioned are as protective coatings, paints or adhesives.

Radiation curing takes place with high-energy light, such as UV light, or with electron beams. Suitable sources for this purpose are, for example, UV lamps having a wavelength range from 240 to 400 nm and an output of from 50 to 240 W/cm.

In the case of electron beams, no photoinitiators are required.

The presence of the novel compound in the radiation-curable compositions makes for ease of application and good leveling of the substrates that are to be coated.

The resulting coatings have good mechanical properties - in particular, good elasticity and flexibility.

Examples

Preparation examples

A) 2,4-diethyl-1,5-octanediol diacrylate

Batch: 326.0 g of 2,4-diethyloctanediol
237.6 g of acrylic acid (10% excess)
193.0 g of cyclohexane
0.6 g of H_3PO_2
0.6 g of triphenyl phosphite
1.8 g of MEHQ (hydroquinone monomethyl ether)
0.2 g of CuCl_2
5.0 g of H_2SO_4

All starting materials were combined and brought to boiling temperature. The time for removal of the water was about 5 h (amount of H_2O = 71 ml).

The product was washed with 6 % strength by weight aqueous sodium chloride solution and with 20 % strength by weight sodium hydroxide solution. Evaporation of the cyclohexane gave a yield of 82.7 %. The viscosity of the product was 15 m Pas.

B) 2,4-diethyl-1,5-octanediol diacrylate ethoxylated with 3 EO

Batch: 252.2 g of 2,4-diethyloctanediol ethoxylated with 3 EO units
114.0 g of acrylic acid (10% excess)
193.0 g of cyclohexane
0.4 g of H_3PO_2
0.4 g of triphenyl phosphite
0.7 g of MEHQ
0.2 g of CuCl_2

7.2 g of p-toluenesulfonic acid, also catalyzable with
 H_2SO_4

All starting materials were combined and brought to boiling temperature. Over the course of 13 h 22 ml of water (theoretical 25.9 ml) were removed.

Subsequent processing was as under A).
Viscosity: 55 m Pas.

C) 2,4-diethyloctanediol-1,5-diacrylate ethoxylated with 7 EO

Batch: 250.0 g of 2,4-diethyloctanediol ethoxylated with 7 EO
units
74.8 g of acrylic acid (10% excess)
193.0 g of cyclohexane
0.3 g of H_3PO_2
0.3 g of triphenyl phosphite
0.7 g of MEHQ
0.2 g of CuCl_2
6.4 g of p-toluenesulfonic acid, also catalyzable with
 H_2SO_4

All starting materials were combined and brought to boiling temperature. Over the course of 13 h 13 ml of water (theoretical 17.2 ml) were removed.

Subsequent processing was as under A).
Viscosity: 55 m Pas

Performance testing

2,4-Diethyl-1,5-octanediol diacrylate (DEODDA) was mixed with different amounts of an epoxy acrylate, and 4 parts by weight of Irgacure 500, based on 100 parts by weight of the mixture, were added as photoinitiator. For comparison, the same epoxy acrylate was mixed with other reactive diluents, namely tripropylene glycol diacrylate (TPGDA) and hexanediol diacrylate (HDDA).

The mixture was applied to a Bonder metal panel in a coat thickness of 100 μm and was irradiated with a total dose of 400 mJ/cm^2 of UV light.

Following irradiation, the Erichsen indentation was measured in accordance with DIN 53156: this is a measure of the flexibility and elasticity. The result is given in millimeters (mm), high values denoting high flexibility.

The results are listed in the table.

| | parts by weight | Erichsen indentation |
|------------|-----------------|----------------------|
| EPA/DEODDA | 50/50 | 4.5 |
| | 60/40 | 4.4 |
| EPA/HDDA | 50/50 | 3.7 |
| | 60/40 | 3.2 |
| EPA/HDDA | 50/50 | 2.0 |
| | 60/40 | 3.1 |

EPA: bisphenol A diglycidyl ether diacrylate

We claim:

1. A compound formed from an alcohol a) and from one or more components b) reactive with the alcohol, wherein alcohol a) is selected from 2,4-diethyloctane-1,5-diol and derivatives thereof alkoxyated with ethylene oxide, propylene oxide or mixtures thereof, and at least one of the components b) reactive with the alcohol is an organic compound b₁) having up to 30 carbons and at least one ethylenically unsaturated, free-radically or cationically copolymerizable group.
2. A compound as claimed in claim 1, wherein the degree of alkoxylation of the OH groups of the 2,4-diethyloctane-1,5-diol is in each case from 0 to 10.
3. A compound as claimed in claim 1 or 2, wherein the organic compound b₁) is acrylic or methacrylic acid.
4. A compound as claimed in any of claims 1 to 3, wherein the compound is a mono- or diester or a mono- or divinyl ether.
5. The use of a compound as claimed in any of claims 1 to 4 as a reactive diluent in a radiation-curable composition.
6. A radiation-curable composition comprising a compound as claimed in any of claims 1 to 4.
7. A process for the radiation-curing of free-radically or cationically polymerizable compositions, wherein the compositions comprise a compound as claimed in any of claims 1 to 4.

Radiation-curable compounds based on 2,4-diethyloctanediol

Abstract

In a compound formed from an alcohol a) and from one or more components b) reactive with the alcohol, alcohol a) is selected from 2,4-diethyloctane-1,5-diol and derivatives thereof alkoxylated with ethylene oxide, propylene oxide or mixtures thereof, and at least one of the components b) reactive with the alcohol is an organic compound b₁) having up to 30 carbons and at least one ethylenically unsaturated, free-radically or cationically copolymerizable group.